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X-Ray Absorption Fine Structure Spectroscopy of Alumina-Supported Copper Oxide for Conversion Electron Yield Detection

In this work, the in-situ x-ray absorption fine structure cell was developed for the conversion electron yield detection to characterize active metal species under reaction gas atmosphere. The probe depth was estimated to be about 9 nm at the Cu K edge. The in-situ conversion electron yield cell was applied to the shape-controlled γ -Al₂O₃-supported Cu₂O catalyst. The reduction to Cu(0) by H₂ of octahedral Cu₂O particles proceeded at lower temperature than cubic particles, indicating that the surface atomic arrangement affects to the redox reaction of solid particles.

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1. Introduction

The x-ray absorption fine structure (XAFS) spectroscopy is a powerful tool to analyze the local structure and electronic state of a target element containing in a large amount of coexisting materials. The utility to dilute samples is quite useful to understand the chemical state of active species of heterogeneous metal catalysts. The electron yield detection for the XAFS spectroscopy achieves the surface sensitive analysis on solid particles. In addition, the applicability under various conditions is a great advantage for the *in-situ* characterization at the operational environment.

The conversion electron yield signal (CEY) is essentially characteristic of atoms confined at or near the probed surface [1]. This specificity is well-suited to deepen the structure obtained in thin layers deposited on absorbing substrates or to follow structural modifications induced by various surface treatments such as ion neutron or electron irradiations, which are depth-limited. Experiments have to be planned taking this CEY depth-dependence into account. This parameter is now relatively well-known and several models can be used to determine its behavior versus the chosen edge and its atomic nature as well as the composition and structure of probed samples [2-4].

However it remains numerous questions about an amplitude reduction frequently observed on EXAFS spectra deduced from CEY when it is compared to a reference one obtained on a transmission device [5-7]. The decrease can be attributed to the detection technique itself which collects all kinds of electrons including those due to the self-absorption of fluorescence photons. The latter are specific to the investigated edge absorption and are emitted during

the decay process [8]. Apart from some very particular configurations - as for instance very low atomic concentration - this signal fraction shows its main failing which consists in a non-linear absorption behavior. EXAFS oscillations can then be modified differently *versus* the probed edge and their subsequent use leads to an erroneous structure modelization. Edge heights specific of the different atomic species which constitutes a sample have to be considered with care before any comparison and use. This last point has already been underlined in previous studies [2] about the alloy composition so obtained.

In this study, we have aimed to combine the electron yield detection with *in-situ* XAFS measurements by developing the *in-situ* XAFS cell for conversion electron yield (CEY) detection. Although a carrier gas of pure He is usually used for the sample atmosphere, the mixing with H₂ and the sample heating have been attempted to achieve the CEY detection under reductive gas atmosphere at elevated temperature.

2. Experimental Work

Figure (1a) shows a design of the newly developed *in-situ* CEY cell for surface sensitive XAFS measurements. The cell body is made of silica glass. A Kapton film (25 μ m thickness) was used as the x-ray window, and an O-ring made of Viton was used to seal between the Kapton film and the cell body. The window was cooled by circulating water to prevent the damage of the O-ring and the Kapton film. A pair of electrodes made of Al to measure sample current was set in a ceramics holder. The sample powder was put on a tilted electrode, and the bias voltage (*ca.* 200 V) was applied to the

other electrode. The highest temperature of the current cell is limited to about 600 °C because of the melting point of Al. The CEY unit can be replaced with the sample holder for transmission measurements, as shown in Fig. (1b).

The shape-controlled Cu₂O particles supported on γ -Al₂O₃ were prepared by the liquid phase reduction method [9]. An aqueous solution of ascorbic acid was dropped into an aqueous solution of CuCl₂, in which the γ -Al₂O₃ powder was suspended. The octahedral Cu₂O particles were available with the average particle size of 325 nm by adding PVP as a surface-active reagent. The cubic particles with the average size of 349 nm were obtained without the addition of PVP. The composition of Cu₂O was confirmed by the XRD measurements, and the particle size was estimated

by the SEM measurements.

The *in-situ* XAFS measurements were carried out at BL-3 of the SR center (Ritsumeikan University), BL-12C of the Photon Factory (KEK), and BL01B1 of SPring-8 (JASRI) at the Cu K edge by using the developed *in-situ* CEY cell. The Si(111) double-crystal monochromator was detuned to remove higher-order harmonics for the measurements at BL-12C, and the Rh-coated double-mirror system was used. The quick-scanning mode was applied for all measurements. The dilute H₂ gas (10 vol% balanced by He, 100 cm³/min) was flowed in the CEY cell, and the powder sample was heated up to 200 °C with the increasing rate of 10 °C/min.

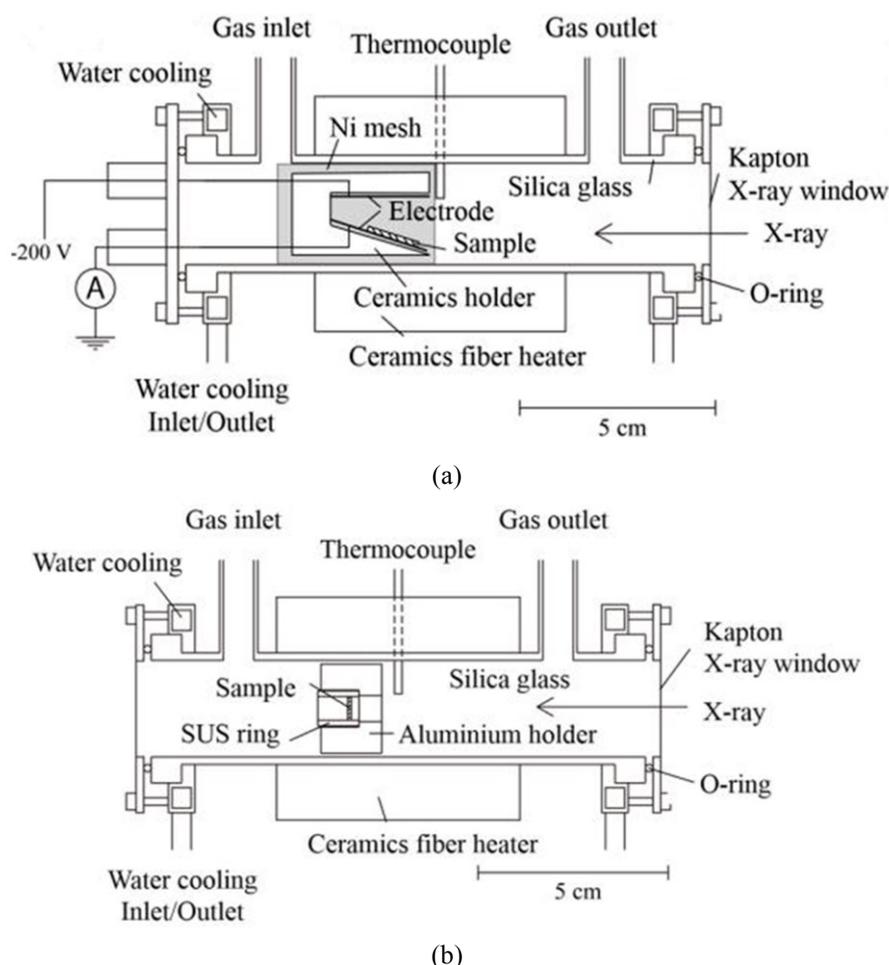


Fig. (1) The schematic diagram of the developed *in-situ* x-ray absorption fine structure cell for conversion electron yield detection (a) and in transmission mode (b)

3. Results and Discussion

The measured XAFS spectra, the EXAFS oscillation functions, and the Fourier transform functions of Cu foil measured by the developed *in-situ* CEY cell are shown in Figure 2 by comparing the results of the transmission mode and the CEY detection. The obtained data by the CEY detection is perfectly in agreement with that of the transmission

mode.

An example of XANES spectral change is shown in Fig. (3) for the reduction process of octahedral Cu₂O particles supported on γ -Al₂O₃ measured by using the *in-situ* CEY cell. The temperature was changed from 25 to 200 °C. The initial and final XANES spectra were respectively consistent with those of Cu₂O and Cu foil measured independently.

The XANES spectrum was changed from Cu_2O to $\text{Cu}(0)$ by increasing temperature under dilute H_2 atmosphere. Some isosbestic points were indicating that the chemical transition from Cu_2O to $\text{Cu}(0)$ proceeded with measured by using the developed *in-situ* CEY no other species. All results indicate that the cell supported Cu_2O particles are reduced for both octahedral and cubic shapes.

The sample composition was analyzed by the pattern fitting of the XANES spectrum, and the calculated values of mole fraction are plotted in Fig. (4) as a function of temperature. In Fig. (4a), the temperature dependence of the composition in the surface region of the particle is compared between octahedral and cubic particles on the basis of the results measured by the *in-situ* CEY technique. The octahedral particles reduced at around 130°C , whereas the reduction of cubic particles proceeded at slightly higher temperature of about 160°C . The lower reduction temperature for the octahedral particle indicates that the (111) facets of the octahedral particle have higher affinity with H_2 than the (100) facets of the cubic particle.

The reduction temperature is compared for the octahedral Cu_2O particle between the CEY and transmission detections. The surface-sensitive CEY detection showed the lower reduction temperature by about 40°C than the bulk reduction probed by the transmission measurement. It is found that the surface region of the octahedral particle is easily reduced because of the existence of the unsaturated Cu atoms on the (111) facet, which strongly interact with the H_2 molecule. Because the O atom migration is necessary for the bulk reduction, the higher temperature detected by the transmission measurement means that the O atom migration occurs at about 170°C in the octahedral particle.

In contrast, the reduction temperature of the bulk region was almost consistent with that of the surface region in the case of the cubic particle, as shown in Fig. (4c). Both measurements showed the comparable temperature of reduction around 170°C . The surface reduction is not facilitated for the cubic particle because of the lack of the unsaturated Cu atoms on the (100) facet. The O atom migration in the Cu_2O particle thus controls the reduction temperature of the whole particle. This motion is independent on the particle shape, and thus the comparable reduction temperatures are reasonable between the octahedral particles with the unsaturated Cu atoms on the surface and the cubic particles with no such Cu atoms.

The CEY measurements revealed that the reduction process of the surface region of octahedral particles was completed at 150°C as seen in Fig. (4). At this temperature, the reduction of about 15 percent of whole Cu_2O particle completed according to the transmission measurement. Because the average size is 325 nm for the octahedral particles, the 15% of the particle volume corresponds to the

shell depth of 8.9 nm . This means that the probe depth by the CEY detection is about 9 nm at the x-ray energy of 9 keV . In the case of the cubic particle, the composition is considered to be homogeneous for all parts of the particle until the reduction is completed, and thus the temperature was observed for both the transmission and CEY detections.

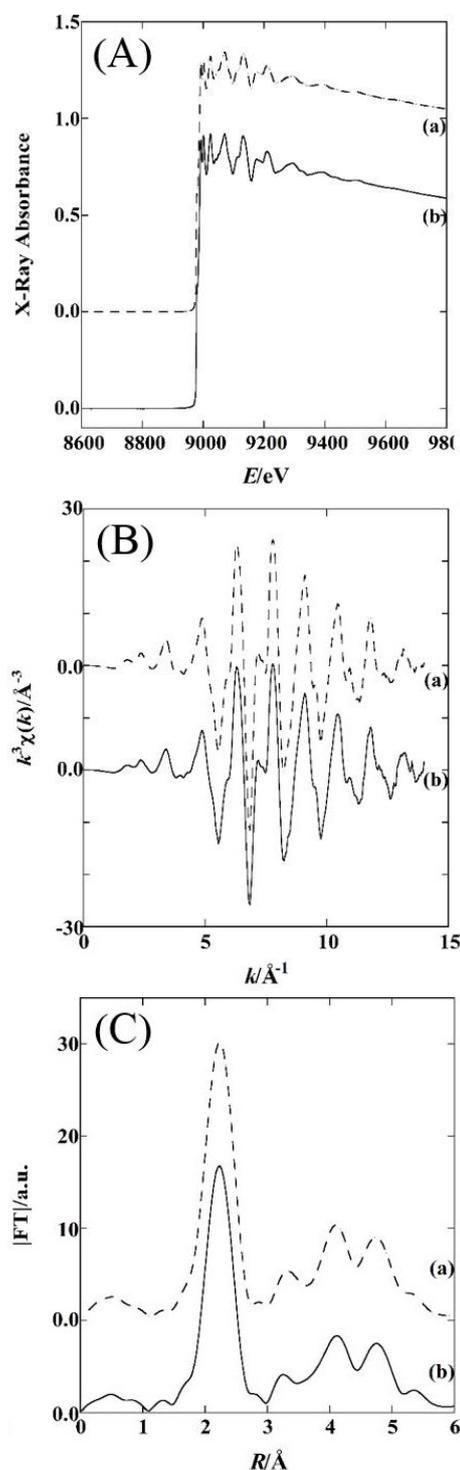


Fig. (2) The x-ray absorption fine structure spectra (A), the EXAFS oscillation functions (B), and the Fourier transform functions (C) of Cu foil measured in transmission mode (a) and by conversion electron yield detection (b)

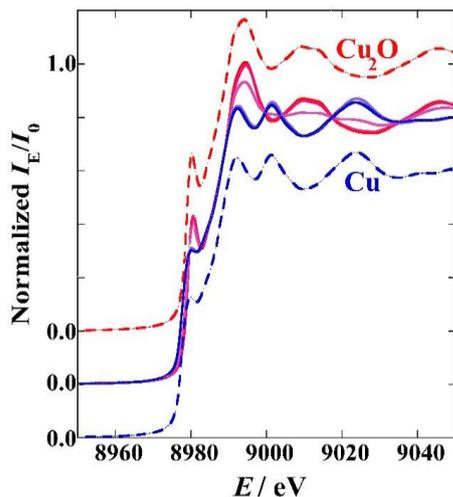


Fig. (3) The XANES spectral change of clearly observed, octahedral Cu_2O particles supported on $\gamma\text{-Al}_2\text{O}_3$

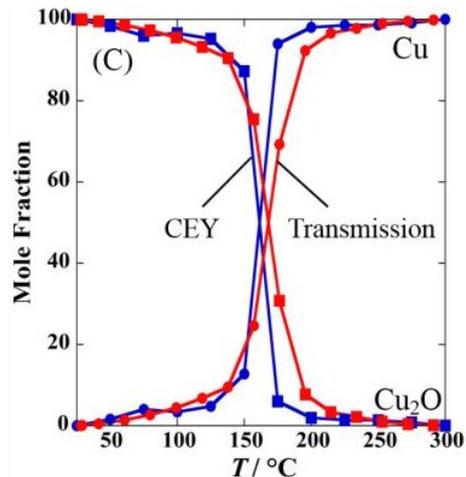
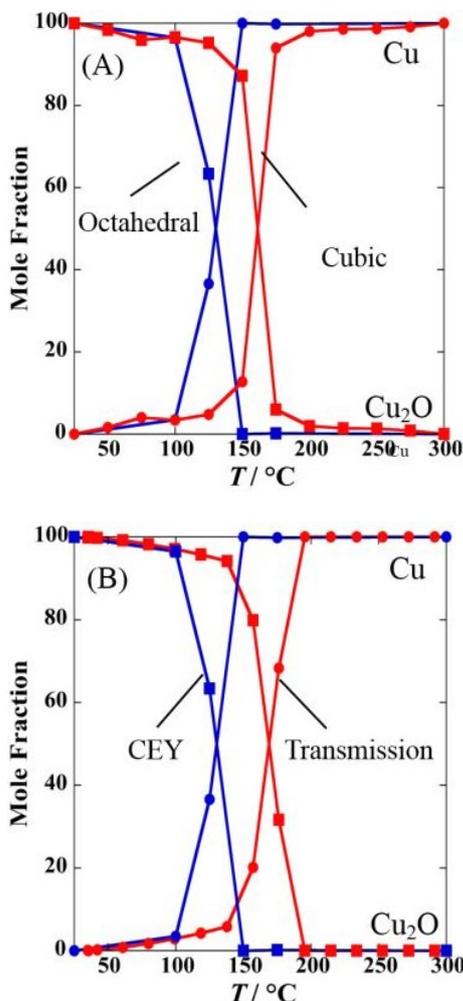


Fig. (4) The mole fraction of Cu_2O and $\text{Cu}(0)$ as a function of temperature for octahedral and cubic particles measured by the CEY detection (a). In (b) and (c), the results of octahedral and cubic particles are respectively compared between the CEY and transmission detection

4. Conclusion

In this study, we have succeeded in developing *in-situ* XAFS cell for the CEY detection with the probe depth of about 9 nm at 9 keV to observe chemical reactions proceeded in the surface region of supported particles in heterogeneous catalysts. The facilitated surface reduction was observed for the octahedral Cu_2O particles, which is supported by the existence of the unsaturated Cu atoms on the (111) facet of octahedral particles. The *in-situ* CEY technique is expected to become a new and useful analysis tool for heterogeneous catalysts.

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